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Properties of concrete using high-lime pfa from a UK source

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Recent changes in UK coal supply have resulted in the production of high-lime ash from a major UK power station. This paper offers results collected during a project to compare the key performance characteristics of concretes using an ASTM class C (high lime) and an ASTM class F (low lime) ash as a partial replacement for Portland cement. Mixes were produced using 40% replacement of Portland cement by weight, with pulverised fuel ash, and a water/cement (w/c) ratio of 0.4. Characteristics examined included workability, compressive strength, water permeability, water absorption, chloride permeability using the rapid chloride permeability test, resistance to sulfate attack, and freeze–thaw resistance. The results showed that the concrete containing the ASTM class C ash was superior in all of these areas except for sulfate resistance. Workability and compressive strength tests were also performed on mixes containing 60, 70, 80 and 90% replacement levels with the class C ash, all with 0.4 w/c ratio. Results showed a steady increase in the workability and a decrease in the compressive strength. Samples made at 90% replacement level showed extreme unsoundness and could not be tested for strength.

1. INTRODUCTION

The use of pulverised fuel ash (pfa) as a partial replacement for Portland cement (PC) in concrete is well known. This reduces the requirement for PC, which is a significant contributor to greenhouse gas emissions, and uses a waste material which would otherwise require disposal in locations such as landfills or surface impoundments.

Pulverised fuel ash has been used in the UK for many years but changes in the coal supply are causing significant changes in the ash. As a result of closures of UK coalmines, substantial quantities of coal are being imported. Continuously changing emission control regulations also have a major influence on the choice of supply. The class C ash used in this project came from one of the main base-load power stations at Rugeley in Staffordshire. The station was designed to burn bituminous UK coals with minimal lime content, but the ash used in this project came from a high lime Indonesian coal. The remainder of the high-lime ash that was not used for this research was sent to land restoration.

Many factors contribute to the performance of concrete containing pfa, one of the most significant of these being the chemical composition of the ash. One method of classification of ashes based on chemical composition is offered by ASTM C618-92a.¹ Ashes are classified as either class C or class F depending on lime content. Due to the pozzolanas present in pfa, high lime content gives the ash cementitious properties. The result of this is that class C ashes can often be used in greater proportions than class F ashes.²

The aim of this work was to study the properties of a high-lime ash from a UK source and to confirm that it conformed to the known properties of similar ashes produced in other countries and to propose beneficial uses for it.

Jiang and Malhotra³ tested several fly ashes of different compositions at 55% replacement. They showed a strong positive correlation between lime content and compressive strength at all ages, although more notably at later ages. Naik *et al.*² noted more rapid development of strength with the use of class C pfa.

Dunstan⁴ noted the effects of the lime content of fly ash on sulfate resistance of concretes and defined the sulfate resistance factor as: $\%CaO - 5/\%Fe_2O_3$, a value below 0.5 showing the ash would improve sulfate resistance.^{5,6} This is credited in many textbooks to the fact that calcium hydroxide is one of the key reactive components when sulfates are present in concrete.⁵⁻⁸

2. EXPERIMENTAL PROGRAMME

An experimental programme was developed in order to compare the performance of concretes mixed with 40% replacement of PC with class C and class F pfa. Tests were then also performed on concrete utilising the class C ash at varying percentage replacement levels in order to determine the effect on performance.

2.1. Ash compositions

The chemical compositions of the ashes used are given in Table 1.

2.2. Mix design

In order to make the results easily comparable the same mix design was used for all samples, varying only the type of ash used and the replacement level of PC with pfa. Details of the mix used for samples of 40% replacement level are shown in Table 2.

Component	Class C ash	Class F ash
	% content	% content
SiO ₂	33.30	46.38
TiO ₂	0.82	1.05
Al ₂ O ₃	14.60	25.25
Fe ₂ O ₃	16.89	8.33
MnO	0.16	0.18
MgO	8.32	2.42
CaO	19.62	5.27
Na ₂ O	0.29	0.88
K ₂ O	1.01	2.08
P ₂ O ₅	0.27	0.64
SO ₃	1.32	0.70
Loss on ignition	3.56	6.33
Total	100.18	99.53

Table 1. Chemical composition of ashes

The cement which is designated PC in this paper was CEM1 to EN 197-1.⁹

2.3. Mixing, casting and curing

Samples were cast according to BS 12390-2¹⁰ and compacted on a vibrating table. They were left under a plastic sheet for 24 h before being de-moulded and left to cure in 21°C lime water until the test date.

3. TEST INFORMATION AND RESULTS

Tests were carried out to measure the workability, strength, water permeability, water absorption, chloride migration, sulfate resistance and freeze-thaw resistance.

3.1. Workability

The workability of the mixes was measured using the slump test (BS 1881 Part 102¹¹). Results for both types of ash at 40% replacement level and the class C ash at 60, 70, 80 and 90% replacement levels are shown in Figure 1.

As can be seen in Figure 1 the mixes containing class C ash showed significantly greater slump than the mix containing class F ash. This may be influenced by carbon content of the ashes.^{4,5} The class F ash showed greater loss on ignition. Alternatively, increased workability may be due to the size/shape of the particles which was not examined. Increasing the replacement level of the class C ash can be seen to increase the workability. This is a well-documented effect of pfa in concrete and is usually attributed to the fineness and spherical nature of the ash particles.^{4,5}

Mix design per m ³	
Content	Weight: kg/m ³
Portland cement	258
Pulverised fly ash	172
Fine aggregate	790
Coarse aggregate	900
Water	180
Total	2300

Table 2. Mix design (40% replacement level of PC with pfa)

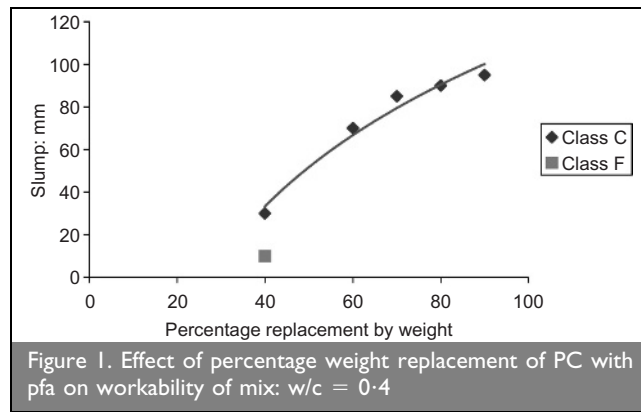


Figure 1. Effect of percentage weight replacement of PC with pfa on workability of mix: w/c = 0.4

3.2. Compressive strength

Compressive strength tests were conducted according to BS 12390-3.¹² Six cubes were tested for each 40% replacement mix and three for each additional mix using the class C ash. Tests were conducted after 7, 14 and 28 days in order to trace comparative developments of strength. Prior to testing the compressive strength, the cubes were measured with a ruler. This offered an approximate check for gross expansion which may have caused unsoundness in the cubes. None was apparent on any of the mixes.

Figure 2 shows the strength development of the mixes containing 40% replacement of PC with pfa. Clearly the class C mix showed higher strengths from a very early age. The lines can also be seen to diverge slightly. The strength development of the mix containing class C ash was more rapid than that containing class F ash. This development possibly indicates pozzolanic reactions being more abundant and beginning earlier in the presence of a higher lime content being available to react with the ash.⁵ Alternatively the increased reactivity may be attributed to finer particles.^{3,5} The higher strength for greater lime contents noted here was also observed by Jiang and Malhotra.³

Figure 3 shows the effects of increasing the pfa content on the compressive strength. As can be seen, the strength abates fairly rapidly. This may be attributed to too much lime leaving an insufficiently reactive phase for reactions to occur. It is notable that adequate strengths were obtained at a 60% replacement level.

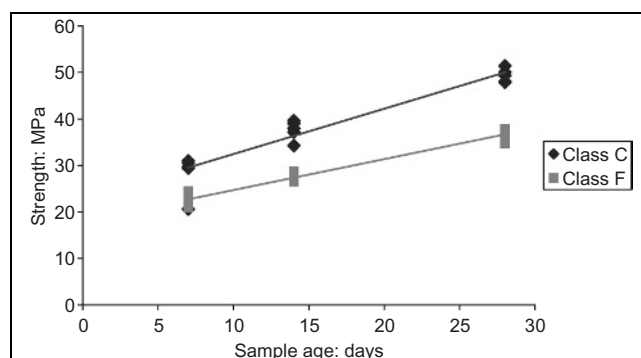


Figure 2. Compressive strength, 40% replacement by weight, w/c = 0.4

$$K = \frac{Vex}{(p_1 - p_2)}$$

where V is the Darcy velocity; e is the liquid viscosity, (0.001 for water); x is the sample thickness (30 mm); p_1 and p_2 are the water pressure before and after the sample (750 and 0 psi) in pascals.

Figure 4 shows the results obtained for the permeability test. The class C ash is less permeable from an early age, again indicating early hydration and reactions filling in the capillary voids and pores. By 28 days the permeability of the two mixes was similar.

3.5. Water absorption

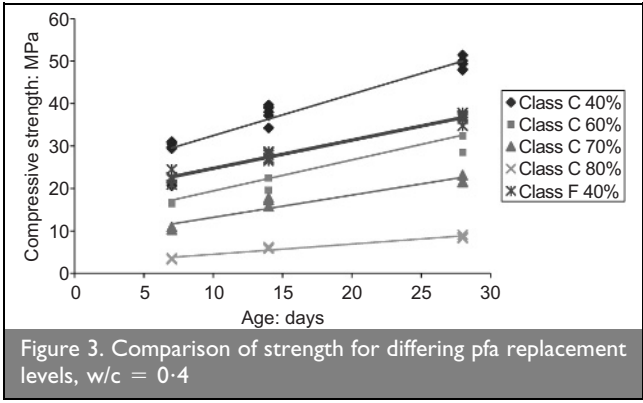
Water absorption tests were conducted to BS 1881-122;¹⁴ however, 100 mm cubes were used for convenience.

Figure 5 shows the results obtained for absorption. As can be seen, the results follow a similar pattern to those for permeability. At early ages the class C ash showed a denser pore structure, with less porosity or smaller pore radius, but by 28 days the results for the two mixes had converged. The slowing of the development of resistance to absorption shown by the curve of the graph was noted by Khatib.¹⁵

3.6 Chloride permeability

Chloride permeability was measured using the rapid chloride permeability test (RCPT) as described in ASTM C 1202-05¹⁶ except that, to prevent overheating, the voltage was reduced to 40 V rather than the 60 V suggested by the standard. The resistivity of the samples was also measured by applying an alternating current. After completion of the RCPT the samples were split through the middle to reveal the cross-section and sprayed with silver nitrate solution to measure the distance migrated by the chloride ions. Samples were tested at 14 and 28 days.

Figures 6 and 7 show the charge passed and resistivity of the concrete samples. A similar resistance to migration was shown at 14 days but after that the results diverged. The samples containing class F ash showed greater resistivity and less charge passed after 28 days. When the results for the silver nitrate test (Table 3) were examined, however, it could be seen that chlorides had migrated a shorter distance in the class C ash samples at 14 days, and similar distances after 28 days. This



3.3. Behaviour of cubes at 90% replacement level

The cubes with 90% replacement of PC with pfa suffered from significant unsoundness, with some collapsing within 60 s of exposure to water. Unsoundness is a known problem with class C ash.⁵ The large molecular volume of the hydrated lime causes high internal pressures which can cause cracking. No unsoundness was noted in the experiments below the 90% replacement level, however.

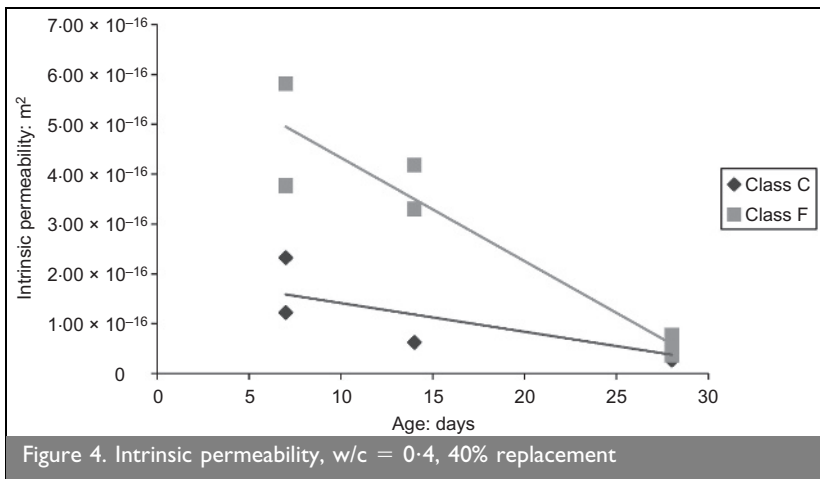
A white build-up occurred on the surface of the 90% replacement cubes. After exposure to phenolphthalein this was shown to be alkaline. It was concluded that this was unreacted hydrated lime (calcium hydroxide), which shows a clear lime excess.

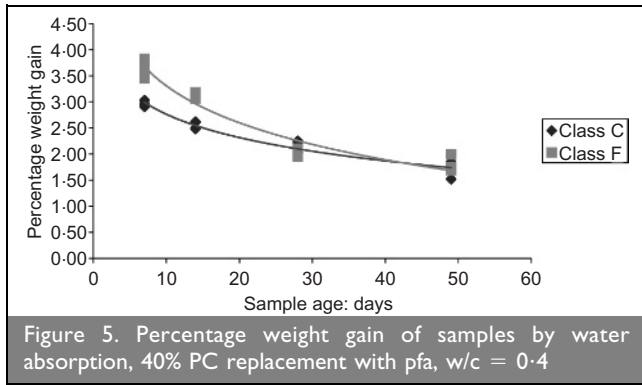
3.4. Permeability

Permeability was measured by pumping water through cylindrical specimen at high pressures while applying a confining oil pressure to prevent leakage around the sides.¹³

Tests were performed on cylindrical samples with a 55 mm diameter and 30 mm length. Water was pumped through the circuit at a pressure of 500 psi (3.4 MPa) while confining oil pressure was set at 750 psi (5.2 MPa).

The time was recorded for 25 ml of water to permeate and be collected in a measuring cylinder. This test was conducted on 40% replacement samples after 7, 14 and 28 days in order to show the development of the permeability/pore structure of the concretes. The intrinsic permeability was calculated using the results and Equation 1.





difference in distances migrated by chlorides for equal charge passed for the two mixes is shown in Figure 8.

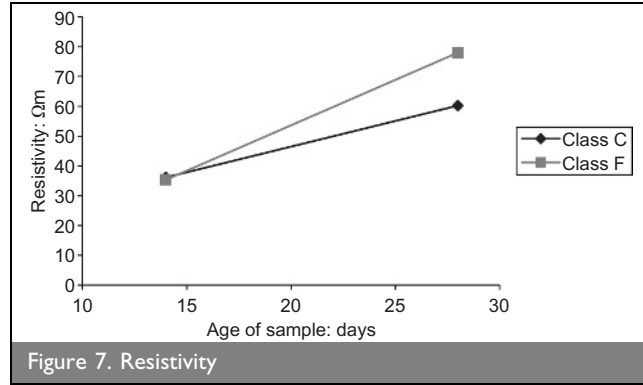
It may be seen that where an equal charge passed through the samples the chloride migration in the class C samples was less. This can be attributed to the increased presence of hydroxyl ions due to increased calcium hydroxide. These ions carry current through the sample and therefore increase the charge, but move more easily than chloride ions and therefore can distort the results of the RCPT test.¹³ When this is taken into consideration it can be said that after 14 days the class C samples were less permeable to chloride migration, and at 28 days both mixes were similar. This is shown by the results of the silver nitrate experiment, which were the only results obtained that rely solely on chloride migration.

These results again follow the pattern shown by permeability and absorption tests, of more rapid development in the samples containing class C ash but convergence around the 28-day age.

Wang *et al.*¹⁷ also conducted the RCPT on class F and class C samples and also noted higher charge passed for class C samples.

3.7. Sulfate resistance

Sulfate resistance was tested by measuring the length change of mortar bars according to ASTM C1012-04.¹⁸ A deviation from the standard occurred in that whereas the standard dictates beginning exposure to the solution once cubes cast of the same mortar reach a compressive strength of 20 ± 1 MPa, bars were exposed at ages of 14 and 28 days regardless of strength.

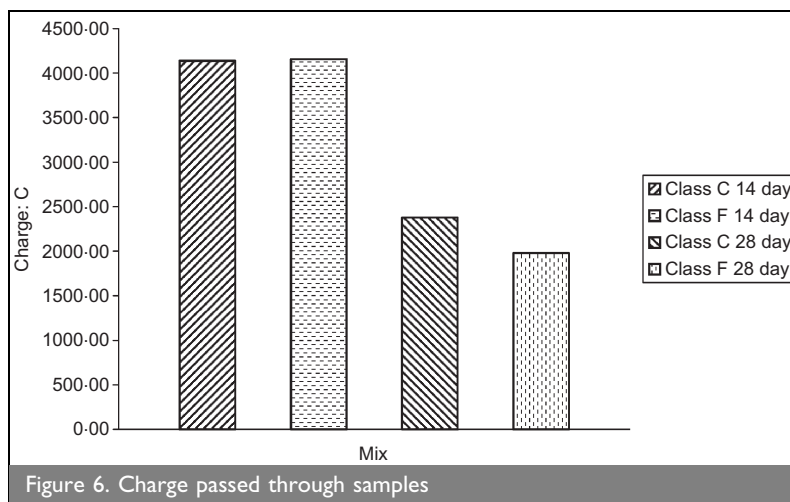


Furthermore, section 7.1 of the ASTM standard, which dictates the mix design of the mortar, was not used. The same mix was used for the mortar as for the concrete with only the coarse aggregate removed. Finally, the expansion of the bars was only measured for 4 weeks due to time restraints (Figure 9).

After 14 days curing the class C samples showed less expansion than the class F samples; however, by 28 days age the class F samples showed less expansion. The class C samples showed greater expansion and therefore less resistance to sulfate attack at 28 days age than at 14 days. Calcium hydroxide is known to be one of the key elements of the reactive phase in sulfate reactions;⁷ the behaviour of the class C mortar bars can be attributed to increased quantities of calcium hydroxide due to continued hydration, which offset the effects of reduced permeability. The length change throughout the test can also be seen to be greater for the class C samples (steeper gradient); this is possibly a result of continued calcium hydroxide production due to continued hydration. This behaviour clearly renders class C ashes unsuitable for use in high sulfate environments.

3.8. Freeze-thaw resistance

In order to test the freeze-thaw resistance, 100 mm cubes were placed in a tray of water 3–5 mm deep and subjected to the freeze-thaw cycle described in ASTM C666-97.¹⁹ The ultrasonic pulse transit time was measured through the samples at intervals, according to ASTM 597-02.²⁰ The results collected were used to calculate the dynamic modulus of elasticity for the samples. Visual inspection of samples was also conducted.



	Class C samples	Class F samples
14 day age	31.6	35.2
28 day age	21	19.5

Table 3. Distance migrated by chlorides as indicated by silver nitrate solution (mm)

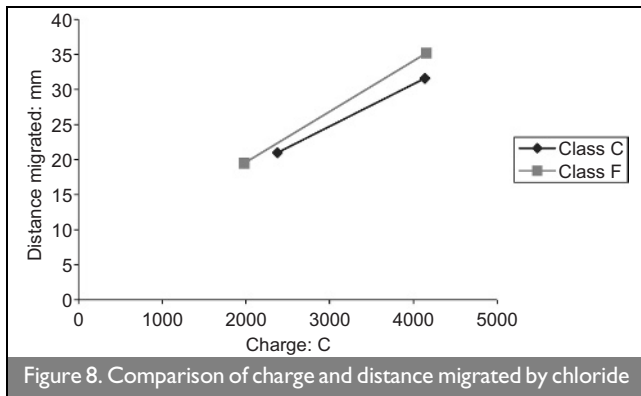


Figure 10 shows the results collected for freeze–thaw resistance. After 14 days the two mixes were fairly similar; however, after 28 days' curing the samples containing class C ash showed a great advantage lasting for around twice as many cycles as the

class F samples. Neither mix used any additives, such as air-entraining admixtures; therefore results can be attributed to the basic concrete properties. These results then show the samples containing class C ash to again have superior strength.

4. DISCUSSION

The results confirm that the class C ash produced in the UK behaved as expected from overseas experience. This material is more reactive and has a greater latent energy than the class F ash and it would therefore be highly desirable to use it rather than waste it. There is also the problem that it is latently hydraulic so it will tend to set when placed in landfill, which may cause operational problems and inhibit land reuse. It is of note, however, that shortly after this sample was taken the station started blending the Indonesian coal with Siberian coal as part of a complex strategy to comply with limits set for sulfate emissions. This reduced the lime content of the ash. Flue-gas desulfurisation is being installed but even with this the very regular quality of ash produced by UK stations in the past is unlikely to occur in the future. In one UK station the desulfurisation process itself is actually producing a high-lime ash.

In order to meet our environmental targets it would therefore be desirable for markets to be developed to suit a range of different ashes which may be produced. The results in this paper show

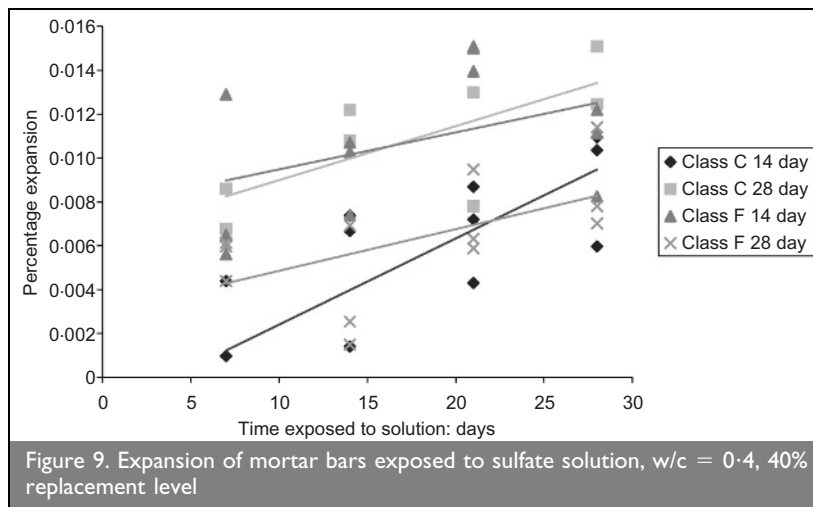


Figure 9. Expansion of mortar bars exposed to sulfate solution, w/c = 0.4, 40% replacement level

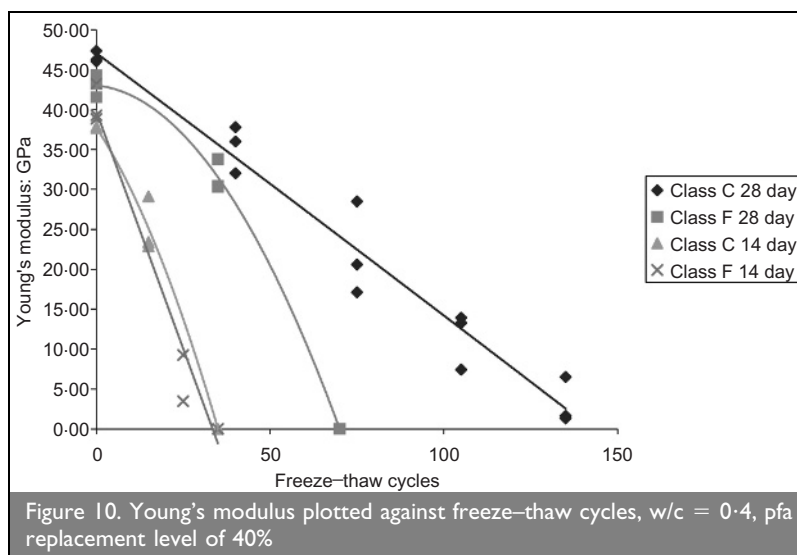


Figure 10. Young's modulus plotted against freeze–thaw cycles, w/c = 0.4, pfa replacement level of 40%

that the ash has good properties except for its sulfate resistance. It is therefore suggested that it could be used for precasting operations for items such as blocks and beams which are going to remain well clear of sources of sulfate, and significant advantage could be gained from the high early strengths.

5. CONCLUSIONS

- (a) High-lime pfa as a partial replacement for PC offers earlier development of strength and pore structure than low-lime pfa. This improves properties such as strength, permeability and absorption at early ages.
- (b) Although the strength of concrete containing high-lime pfa remains superior to that containing low lime at 28 days age, other properties such as permeability, permeability to chlorides, and absorption may be similar regardless of lime content.
- (c) High-lime ash is unsuitable for environments with significant presence of sulfates.
- (d) High-lime pfas can be used to replace a greater proportion of PC than low-lime pfas; up to 60% replacement by weight appears feasible for applications with lower strength requirements.

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